IN-LINE SPECTROMETER

CLAIM OF BENEFIT TO PRIOR PROVISIONAL APPLICATION

This application claims benefit to U.S. Provisional Patent Application 60/454,588, filed on 3/13/03, which is incorporated herein by reference.

BACKGROUND

Fluorescence occurs when a substance receiving a light of a certain color (excitation) emits a light of a different color (emission). The wavelength of the emission is typically longer than that of the excitation. A fluorometer is a device that measures fluorescence by supplying an excitation source, detecting the resulting emission, and converting the emission into an electrical signal proportional to fluorescence. This electrical signal can be used to drive a display to show the fluorescent signal and/or used as a control signal for controlling processes. There are various implementations of fluorometers. A spectrofluorometer allows the user to select the excitation and/or emission wavelengths. A scanning spectrofluorometer can scan the excitation and/or emission over a range of wavelengths.

Fixed filter fluorometers are used when low cost and/or reliability are desirable. Fixed filter fluorometers have a light source with an optional filter to select an optimal excitation wavelength. The detector also has a filter to select the optimal emission wavelength, which is different from the excitation wavelength. Typically, the excitation source and the emission detector are positioned at a 90° angle from each other, though this may change depending on the application.

Fluorometers are used in a wide variety of applications, including but not limited to environmental studies, leak detection, dye tracer studies, and industrial control. In industrial control applications, an inert fluorescent tracer is bonded with a control chemical of interest (for example, a biocide to prevent biological growth within a cooling system). The quantity of the

fluorescent tracer is directly proportional to the control chemical. As the control chemical is consumed the amount of fluorescent tracer will drop. Using a fluorometer to detect the amount of fluorescent tracer allows the user to indirectly measure the control chemical. Using this fluorescent measurement the user can accurately control the amount of control chemical in the system. This can be as simple as turning on a pump when the fluorescent signal drops to a certain level (thus adding the control chemical to the system) and turning off the pump when the fluorescent signal reaches a desired level. More complex algorithms can be used as well.

A limitation of current fixed filter fluorometers for industrial control is that they must be supplied a water stream from the system of interest. Additional plumbing must be installed, usually with safety features, to supply water to the fluorometer and to either return the water to the system or dispose of it. This additional plumbing adds cost, labor, and complexity to the system. These fluorometers usually have a flow cell, which is a clear tube through which the sample water flows so that the fluorescence can be detected. This flow cell can become fouled (become less optically clear) which reduces the fluorescent signal. If the flow cell remains fouled then an error is introduced into the control of the system. Since this is undesirable, a periodic maintenance is usually required to clean the flow cell, again adding undesirable labor and cost. An example of such a fluorometer is described in USP 6,369,894.

Therefore, there exists a need for a fluorometer that can be introduced directly into a stream of non-solid material. This greatly reduces the installation requirements for the fluorometer and eliminates the flow cell, thus reducing maintenance requirements. More generally, there is a need for a spectrometer that can easily be introduced into a stream of a non-solid material.

SUMMARY

Some embodiments of the invention provide an improved spectrometer that measures light emissions and/or reflection from a non-solid material that flows through a system of pipes. This spectrometer is designed to fit into a standard pipe system. The material flows past a distal end of the spectrometer that is inserted in the pipe system. The spectrometer has the ability to project light onto the material and collect a resulting light from the material through the distal end as the material flows past this end.

DESCRIPTION OF THE DRAWINGS

The novel features of the invention are set forth in the appended claims. However, for purpose of explanation, several embodiments of the invention are set forth in the following figures.

Figure 1 is an outside view of the fluorometer.

Figure 2 is an exploded view of the preferred embodiment of the fluorometer.

Figure 3 is a cross-sectional view of the preferred embodiment of the fluorometer.

Figure 4 is a detailed cross-sectional view of the optical end of the fluorometer.

Figure 5 is a block diagram of the electronics in the fluorometer.

Figure 6 is a view of the fluorometer mounted in an installation tee fitting.

Figure 7 is an exploded view of the fluorometer mounted in an installation tee fitting.

Figure 8 is a view an alternative mounting of fluorometer in an installation tee fitting.

Figures 9 and **10** illustrate two other fluorometers of some embodiments of the invention.

Figure 11 illustrates a process for calibrating the fluorometer.

DETAILED DESCRIPTION

In the following description, numerous details are set forth for purpose of explanation. However, one of ordinary skill in the art will realize that the invention may be practiced without the use of these specific details. In other instances, well-known structures and devices are shown in block diagram form in order not to obscure the description of the invention with unnecessary detail.

Figures 1-3 illustrate a fluorometer 50 of some embodiments of the invention. **Figure 1** illustrates a perspective view of the outside of the fluorometer 50 as seen by the user, **Figure 2** illustrates an exploded view of the fluorometer 50, and **Figure 3** illustrates a cross-sectional view of the fluorometer 50. This fluorometer is designed to fit into a standard pipe system and measure the fluorescence of a non-solid material (e.g., a liquid, vapor, etc.) flowing through this system. The material flowing through the pipe system is water in the examples described below. However, one of ordinary skill will realize that the invention's fluorometers can be used to gauge the fluorescence of any non-solid material (e.g., any liquid or vapor). Also, even though several fluorometers are described below, several aspects of the invention are applicable to other types of spectrometers, such as turbidimeters.

As shown in these figures, the fluorometer 50 includes a tube housing 100, a collar 105, an electrical cable 110, two fiber optic cables 115 and 120, a cap 125, an optical coating 130, o-rings 305, an emission filter 315, sleeves 320 and 335, a photodiode 325, an excitation filter 330, a light emitting diode (LED) 340, a printed circuit board (PCB) 350, a metal shield 355, and an optical chassis 365.

The tube housing 100 houses several components of the fluorometer, such as fiber optic cables 115 and 120 and the PCB 350, which houses the electronic circuitry of the fluorometer. This housing is made of a water resistant material, such as PVC or delrin, although other plastics or metals could be used depending on the possible chemical interactions between the material

and the process water. Collar 105 is provided to set the height of the tube housing, and thereby set the proper height of the fluorometer in the process water. This collar also provides a sealing surface when the fluorometer is mounted in an installation tee fitting, as further described below.

Cable 110 is a cable connection that includes several conductors (e.g., several wires). Power is supplied to the fluorometer through cable 110. Optional control lines that can change the sensitivity and dynamic range of the fluorometer can also be supplied to the fluorometer 50 through cable 110. Cable 110 also provides a signal out that is proportional to fluorescence. This signal can be either (1) an analog signal (for example, 0 to 5 volts or 4 to 20 ma) that can be detected by typical industrial controllers, or (2) a digital output that can be read by computers or computer based controllers.

Cap 125 provides a sealing surface to prevent water from entering the fluorometer. Cap 125 also has two orifices 370 and 375 that contain two fiberoptic cables 115 and 120. Fiberoptic cable 120 carries the excitation light from the light source to the water, while fiberoptic cable 115 carries the resulting emission light (produced by the liquid in response to the excitation light) to the detector. At the distal end of the fluorometer 50, the fiberoptic cables 115 and 120 are both set into cap 125 at an approximately 20° angle with respect to a vertical axis of the cap, as shown in **Figure 4**. As further shown in this figure, these settings result in about a 40° angle between the two fiberoptic cables. When light leaves the beveled end of cable 120 and enters the water, the actual angle of the light is closer to 45° due to the angle of incidence and the difference in density between the fiberoptic and the water. Similarly, the emission light collected by the fiberoptic cable 115 is closer to 45°. This approximately results in an optimal 90° between the excitation and the emission. Since the two fiberoptic ends are close to each other, the measured sample is quite small, which means the angles of the fibers are not very critical in this embodiment.

As shown in **Figures 1** and **3**, an optically clear coating 130 is applied to cap 125 and the

ends of orifices 370 and 375 and fiberoptic cables 115 and 120. This optical coating 130 provides a seal around the fiberoptic cables 115 and 120 and the cap 125 and provides protection for the fiberoptic cable ends. This coating 130 (typically an epoxy) gives a smooth finish that is easily wiped clean. If ever abraded, the epoxy could be polished to once again give an optically clear finish.

Cap 125 is inserted into the tube housing, and the o-rings 305 provide sealing about the cap to prevent water from entering the fluorometer. The fiberoptic cables 115 and 120 travel through the orifice 370 and 375 of the cap 125. As shown in **Figure 3**, the cables 115 and 120 travel through the chambers 370 and 375 initially at the 20° angle with respect to the vertical axis and then in parallel to this axis. The fiberoptic cables 115 and 120 then each pass through the optical chassis 365. The optional excitation filter 330 is placed between the end of the fiberoptic cable 120 and the light emitting diode (LED) 340 to select an optimal excitation wavelength of the light emitted from the LED. The sleeve 335 centers and retains the LED 340 so the maximum amount of light is transmitted into the fiberoptic cable 120.

The emission filter 315 is placed between the fiberoptic cable 115 and a photodiode 325. The emission filter selects the optimal emission wavelength, which is typically different from the excitation wavelength. The photodiode 325 detects the emitted light that is transmitted through the fiberoptic cable 115. Photodiode 325 is secured and centered by sleeve 320. Sleeve 320 may also provide electrical isolation between the case of the photodiode 325 (if the case is metal) and optical chassis 365 (if the chassis is constructed from metal).

Figures 2 and **3** also show that LED 340 and photodiode 325 are connected to the PCB 350. In order to prevent electrical noise from entering the pre-amplifier section of the PCB 350, the metal shield 355 covering the pre-amplifier circuitry is attached to the PCB 350 and grounded. The electrical cable 110 is soldered to PCB 350. Finally, the top of the instrument is sealed using potting material 300, though a cap similar to cap 125 could be used with a water

tight connector.

Figure 5 is a block diagram of the circuitry internal to the fluorometer and contained on PCB 350. Power provided to the fluorometer is conditioned and converted by power circuitry to provide the necessary voltages for the fluorometer circuitry. LED circuitry 405 controls the LED 340, flashing it alternately ON then OFF. When the LED circuitry 405 turns ON LED 340, excitation light from LED 340 is first filtered by filter 330 and then directed towards the water passing by the distal end of the fluorometer 50 that is inserted into the plumbing. When LED 340 is ON, the fluorescence of the water stream will produce an emission light that combines with the ambient light. When LED 340 is OFF, only ambient light will be present.

The ambient light and/or emission light produced by the excitation is picked up by fiber optic cable 115, which routes this light to the photodiode 325 through the emissions filter 315. The photodiode 325 generates a current, which is converted to a voltage and amplified by a pre-amplifier circuitry 410. The output of the pre-amplifier becomes the input for the ambient light rejection circuit 415.

The ambient light rejection circuitry 415 receives the same signal as LED 340 from the LED driver circuitry 405. By synchronizing to this signal, the ambient light rejection circuit 415 can determine whether it is examining excitation light plus ambient light (when LED 340 is ON) or just ambient light (when LED 340 is OFF). When the LED 340 if OFF, the ambient light rejection circuit 415 detects the amount of ambient light that is picked up by the photodiode 325. Subsequently, when the LED is ON, this rejection circuit 415 discards the detected ambient light contribution from the signal that it receives from the pre-amplifier circuit and that is based on the ambient and emission light detected by the photodiode. In other words, when the LED is ON, the rejection circuit subtracts the ambient light signal from the excitation plus ambient light signal to obtain a signal that is only dependent on the excitation light.

A variable amplifier circuit 420 that is controlled by gain control signals 445 amplifies

the output of the light rejection circuitry 415. The variable amplifier circuit amplifies, for example, by a factor of 10, 100, or 1000 to give the user choices in the sensitivity and dynamic range of the fluorometer. The resulting 0 to 5 volt output 450 can be routed to cable 110 where an external controller can use it for control purposes. Alternatively, the 0-5 volt can be converted to alternative outputs. For example, it can be converted to a 4 to 20 ma signal by a voltage-to-current converter circuit 425. Another alternative is to convert the 0 to 5 volt output 450 to a digital signal with an Analog to Digital converter 430. This digital output can then be read by a microcontroller 440, processed internally, and reported as a serial data signal 455 to a computer through cable 110. When microcontroller 440 is used, it can automatically control the gain control lines 445 to the final amplifier circuit 420, which gives the advantage of both excellent sensitivity and a large dynamic range. Alternatively, as shown in **Figure 5**, a user can manually adjust the gain control signal on the gain control line 445 in some embodiments.

In operation, power is supplied to the fluorometer through cable 110. The output signals 450, 435, and 455 are also connected to an external controller (e.g., a computer) through cable 110. These output signals are proportional to fluorescence. Therefore, an external controller can use these output signals to drive a display to show the fluorescence of the liquid and/or to control in an automated fashion a chemical process that is monitored through the fluorescence detection.

As mentioned above, the gain control signals 445 can also connected through the cable 110 to a user or an external controller. The devices 400-430 and 440 that are illustrated in **Figure 5** are in one or more IC's that are positioned on the PCB 350. These IC's are illustrated in **Figure 2** as rectangular boxes on the PCB 350.

In some embodiments, the fluorometer 50 is designed to fit into a standard plumbing installation tee that is often found in industrial piping. **Figures 6** and **7** illustrate one such fitting. Specifically, **Figure 6** shows the fluorometer mounted in an installation tee 200, while **Figure 7** shows an exploded view of this fitting. **Figure 6** illustrates that the installation tee fitting 200 is

inserted into a pipe system, so that a pipe 215 in this system supplies process water to the tee, while another pipe 220 in this system delivers the process water from the tee to another destination in the pipe system. As shown in **Figures 6** and **7**, the fluorometer is inserted into the installation tee fitting 200 and an o-ring 210 is placed between the collar 105 and the installation tee fitting 200 to prevent water leakage. Cap 205 is installed to squeeze collar 105 and installation tee fitting 200 together which compresses o-ring 210, forming a water tight seal and holding the fluorometer securely in place, as shown in **Figure 6**.

An alternative way for installing the fluorometer is shown in **Figure 8**. In this embodiment, housing 100 is threaded at the end of the optical cap. The installation tee 250, which is used in this embodiment, has corresponding threads to accept the fluorometer. This embodiment has the advantage of using an installation tee 250 that is commonly found in plumbing systems thus making installation of the fluorometer easier for the user. Several variations of installation tee 250 exist. In one such variation, the tee 250 changes the direction of the water by 90° angle. In other words, in this tee, the angle between the pipe that brings the water into the tee and the pipe that takes the water out of the tee is 90°. The fluorometer can be placed in this tee in a chamber that is collinear with one of the pipes connected to this tee.

In some embodiments, the fluorometer is calibrated before its first operation. **Figure 11** illustrates a process 1100 for this calibration. As shown in this figure, the calibration process starts by providing (at 1105) two known samples to the fluorometer, typically a blank or zero reading plus a known dilution. Since the fluorometer includes ambient light rejection, the user need not be concerned with interference from the surrounding light. The user then places (at 1110) the fluorometer into the first blank solution in a first container and programs (at 1115) the controller to interpret the output from the fluorometer as zero. The user then places (at 1120) the fluorometer in a second container that has the second solution with known concentration, for example 100 parts per billion (ppb); the second container can be the same as the first container

except that it has to be cleaned after removing the first solution before inserting the second solution. The user next programs (at 1125) the controller to interpret this output as 100. In most cases this is adequate since the fluorescent signal is linear with respect to the concentration. If the response is non-linear, many industrial controllers allow a multipoint calibration.

Once the fluorometer is calibrated, it is ready to be installed in the process stream. Water is shut off to the pipe by means of a valve. The covering cap from the installation tee fitting 200 is then removed and the fluorometer is inserted in the tee in a water-tight fit that is accomplished through a cap (such as cap 205 as shown in **Figures 6** and **7**) or through threading on the fluorometer and in the tee (as shown in **Figure 8**). The process water is then returned to the pipe. If fouling occurs on the fluorometer (potentially reducing the signal), the fluorometer is removed, cap 125 is wiped clean, and the fluorometer reinserted.

The fluorometer excites the sample water with light from LED 340. The resulting emitted light is detected by photodiode 325. The circuitry on PCB 350 conditions and amplifies the signal from photodiode 325 and produces a signal proportional to fluorescence. A controller (not shown) can then use the signal from the fluorometer to turn on a pump to add more chemical when the fluorescent signal indicates the concentration is too low, and turns off the pump when the concentration reaches an upper limit.

Some embodiments have fiber optic cables 115 and 120 of the fluorometer 50 as short as possible (e.g., have these cables at 1 to 2 inches). This results in the electronics being close to the water stream. In applications where it is desirable for the electronics to be remote to the water stream (for example, if the water is extremely hot or even steam) then the fiber optic cables can be extended, such that the electronics is outside of the installation tee fitting. This allows the electronics to remain closer to ambient temperature even under extreme sample conditions.

The fluorometer 50 has several advantages. For instance, it can easily be installed in existing plumbing systems to measure a process water stream, or some other liquid stream. It

also requires much less maintenance. Its maintenance is also much easier to perform as it can be easily removed and/or replaced from the plumbing system.

Figures 9 and **10** show two other fluorometers 900 and 1000 that are used in some embodiments of the invention. These figures simply show these fluorometers' distal ends (which are to be inserted in the pipe system) to illustrate the differences between these fluorometers and the fluorometer 50 that was described above. **Figure 9** illustrates a fluorometer 900 that is similar to the fluorometer 50 except for the position of its LED 340 and filter 330 and for its lack of a fiber optic cable 120. Specifically, in the fluorometer 900, the LED 340 and filter 330 are moved next to the distal end of the orifice 375 in the cap 125. The LED receives a drive signal from the LED driver circuit 405 through a conductor 905. Through the orifice 375 and filter 330, light emanates from the LED 340 onto the liquid passing by the distal end of the fluorometer that is inserted into the plumbing. As the LED 340 is moved close to the distal end of the orifice 375, there is no need for a fiber optic cable 120 to carry the light from the LED to the water. Hence, the fluorometer has no such cable.

Like the end of the fiber optic cable 120 in the fluorometer 50, the LED 340 in the fluorometer 900 is placed at an angle (e.g., 20°) with respect to the vertical axis of the the cap 125, as shown in **Figure 9**. This placement of the LED results in about a 40° angle between the LED and the fiberoptic cable 115 in the fluorometer 900. When light leaves the LED and enters the water, the actual angle of the light is closer to 45° due to the angle of incidence and the difference in density between the fiberoptic and the water. Similarly, the collected emission light into fiberoptic cable 115 is closer to 45°. This approximately results in an optimal 90° angle between the excitation and the emission. Since the fiberoptic cable 115 and the LED 340 are so close to each other, the measured sample is actually quite small, which means the angles are not very critical.

Figure 10 illustrates a fluorometer 1000 that is similar to the fluorometer 50 except for the position of its LED 340, photodiode 320, and filters 315 and 330, and for its lack of fiber optic cables 115 and 120. Like the fluorometer 900, the LED 340 and filter 330 in fluorometer 1000 are moved next to the distal end of the orifice 375 in the cap 125. However, unlike the fluorometer 900, the photodiode 325 and filter 315 are also moved next to the end of the orifice 370 in the cap 125. Through the orifice 370 and filter 315, the photodiode 325 receives light emitted off the liquid passing by the distal end of the fluorometer that is inserted into the plumbing. The photodiode 325 converts this light to a current that is passed to the pre-amplifier circuit 410 along a conductor 910. As the photodiode 325 is moved close to the distal end of the orifice 370, there is no need for a fiber optic cable 115 to carry the light from the orifice 370 to the photodiode. Hence, the fluorometer 1000 has no such cable.

Like the end of the fiber optic cable 115 of fluorometer 50, the photodiode 325 of fluorometer 1000 is placed at an angle (e.g., 20°) with respect to the cap 125, as shown in **Figure 10**. Also, in some embodiment, the photodiode 325 of fluorometer 1000 of **Figure 10** has a lens to provide a narrow acceptance angle for light, in order to achieve an angle for receiving light close to the desired 20° angle. This lens along with the placement of the photodiode results in about a 40° between the LED 340 and the photodiode 325. When light leaves the LED and enters the water, the actual angle of the light is closer to 45° due to the angle of incidence and the difference in density between the fiberoptic and the water. Similarly, the emission light gathered by the photodiode 325 is closer to 45°. This approximately results in an optimal 90° angle between the excitation and the emission. Since the photodiode 325 and the LED 340 are so close to each other, the measured sample is actually quite small, which means the angles are not very critical.

Both of the fluorometers 900 and 1000 share the benefit of eliminating a junction between fiber 120 and filter 330, while the fluorometer 1000 also eliminates the junction between fiber 115 and filter 315. Junctions such as these typically result in loss of light and therefore less sensitivity to fluorescence. However, placing components at the face of the instrument increases the instrument diameter, or requires smaller sized LED 340, photodiode 325, and/or filters 330 and 315, which in turn reduces the instrument's ability to generate excitation light and capture emission light.

While the invention has been described with reference to numerous specific details, one of ordinary skill in the art will recognize that the invention can be embodied in other specific forms without departing from the spirit of the invention. For instance, in the embodiments described above, the orifices 370 and 375 are placed on the same side of the distal end of the fluorometers. However, in other embodiments, these orifices can be placed on different sides of the distal end of a fluorometer. Alternatively, these orifices can be placed on different locations of a curved surface of the distal end of a fluorometer (e.g., can be placed at opposing locations on a cylindrical or semi-spherical surface of the distal end). Yet other embodiments might only have one orifice at the distal end of the fluorometer. Through this one orifice, these embodiments might project and collect light.

Several fluorometers were described above. However, one of ordinary skill will realize that some embodiments of the invention are spectrometers that use the features described above for the invention's fluorometers. For instance, some embodiments of the invention are turbidimeters that are similar to the fluorometers 50, 900, and 1000, except for their filters 315 and 330. As mentioned above, fluorometers emit light of a certain color and receive a light of a different color. Accordingly, in a fluorometer (such as fluorometer 50, 90, or 1000) the filter 315 is different than the filter 330 (i.e., the filter 315 allows light of a different wavelength to pass through than the filter 330). On the other hand, a turbidimeter emits and receives light of the

same color. Hence, the filters 315 and 330 of a turbidimeter of some embodiments would be similar (i.e., would allow the same wavelength of light to pass through). Other than having to using matching filters 315 and 330, the turbidimeters of some embodiments are identical to the fluorometers described above. Hence, the schematics illustrated in **Figures 1-11** above are equally representative of the turbidimeters of some embodiments of the invention. Thus, one of ordinary skill in the art will understand that the invention is not to be limited by the foregoing illustrative details, but rather is to be defined by the appended claims.